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2. Ion chemistry of  $\text{HBr}^+$
3. Measurement of vibrational lifetimes (Einstein A)
4. Proton affinity measurements

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OWEN R. COTE  
Chief, Geophysics and Space



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Chief Scientist\*

USAF 180189

VIBRATIONALLY EXCITED IONS; QUENCHING, LIFETIMES

Report on USAF research grant.

This grant was provided under an emergency procedure to enable a successful collaboration between Dr. Eldon Ferguson at Universite de Paris-Sud and U.C.W. Aberystwyth to continue when the Aberystwyth SERC support failed for a period of 9 months. (category alpha but unfunded!) SERC support was renewed in October 1988. The USAF support came too late to enable me to employ Dr. R. Richter from Professor W. Lindingers laboratory at Innsbruck but it was invaluable in that it enabled us to re-start our measurement programme by providing gas supplies etc.

The collaboration between Paris-Sud and Aberystwyth has now been going on for nearly two years and has produced a number of new developments and several publications (2 papers published, 2 submitted and 2 in advanced state of preparation plus 2 conference papers (SASP and ESCAMPIG) a total of 8 papers).

Vibrational quenching studies

1. HCl<sup>+</sup> (v=1) and DCI<sup>+</sup> (v=1)

The vibrational quenching of HCl<sup>+</sup> (v=1) and DCI<sup>+</sup> (v=1) ions in collisions with Ar and Kr have been measured in order to investigate the effect of changing the vibrational and rotational energy levels while keeping the intermolecular interaction potential unchanged. The results tend to disapprove the modified Landau-Teller type vibrational quenching mechanism. Published: Chem. Phys. Letts. 144, 131-5, 1988.

2. In the course of the above investigation measurements of the reaction HCl<sup>+</sup> + SF<sub>6</sub> and HCl<sup>+</sup> + CF<sub>4</sub> provided improved data on AE (SF<sub>6</sub><sup>+</sup>/SF<sub>6</sub>) and AE (CF<sub>4</sub><sup>+</sup>/CF<sub>4</sub>). Published Int. J. Mass Spec. & Ion Proc. 79, 231-5, 1987.

3. HBr<sup>+</sup> and DBr<sup>+</sup>

Efforts to extend the above study to HBr<sup>+</sup> (DBr<sup>+</sup>) was frustrated by the fact that the ground state spin orbit splitting is comparable to the vibrational spacing. We could achieve success if we develop an ion source which produces only (<sup>2</sup>Π<sub>1/2</sub>) ground state ions. The opportunity was taken to do the HBr<sup>+</sup> ion chemistry and this showed the existence of a stable FHBr molecule with D(HF-Br) > 0.2eV. (HBr<sup>+</sup> ion chemistry to be submitted Int. J. Mass Spec. and Ion Proc).

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#### 4. Measurement of vibrational lifetimes (Einstein A coefficient)

A flow tube method of measuring vibrational lifetimes has been developed at Aberystwyth and applied to the case of  $\text{HCl}^+(\nu=1)$  and  $\text{DCl}^+(\nu=1)$ . The result for  $\text{HCl}^+$  is in excellent agreement with a theoretical value while the experimental  $\text{DCl}^+$  value is somewhat lower than theory. (To be submitted to Int. J. Mass Spec. & Ion Proc).

#### 5. Proton Affinity measurements

In a collaboration with Professor D. Smith and Dr. N.G. Adams at Birmingham an improved proton affinity scale has been established in the 130-140 kcalmol<sup>-1</sup> range ( $\text{CF}_3$  to  $\text{CO}$ ). Submitted to J. Chem. Phys.

6. A study of several forward and backward proton transfer reactions in the Aberystwyth SIFDT has demonstrated that this method is capable of providing good data on enthalpy and entropy changes in such reactions. Since the enthalpy change = the proton affinity difference, a proton affinity scale can be generated. These results reverse the previously held view that a SIFDT apparatus would be unsuitable for studies because of the lack of thermodynamic equilibrium. This earlier view was based on a reaction involving  $\text{N}_2\text{OH}^+$  but the conclusions were in error because of the existence of two isomeric forms of  $\text{N}_2\text{OH}^+$ . This new development is important because the SIFDT method can be used over a very much larger energy range than a variable temperature SIFT apparatus. In consequence this implies that much larger P.A. differences can be investigated. Two publications: Submitted to Int. J. Mass. Spec. and Ion Proc. and to Chem. Phys. Letts.

In summary a very productive collaboration. Clearly not all this work was completed in the 9 months support period provided by the USAF award but it provided invaluable support at a critical period. Thank you very much. This will be acknowledged in the published papers.

N.D. Twiddy.

*N.D. Twiddy* 24/1/89.

HCl<sup>+</sup>(v=1) AND DCl<sup>+</sup>(v=1): (i) VIBRATIONAL QUENCHING BY Ar AND Kr

(ii) RADIATIVE LIFETIMES

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Both the vibrational quenching of HCl<sup>+</sup>(v=1) and DCl<sup>+</sup>(v=1) and the radiative lifetimes of these vibrationally excited ions have been measured in a selected ion flow tube SIFT using a monitor ion technique<sup>1,2</sup>. The monitor gas employed in both studies was N<sub>2</sub> since this proton transfers with HCl<sup>+</sup>(v>0) and DCl<sup>+</sup>(v>0) but is endoergic for both ions in the ground state<sup>3</sup>. Thus the vibrationally excited species population is monitored by the N<sub>2</sub>H<sup>+</sup> (N<sub>2</sub>D<sup>+</sup>) signals. For the quenching studies<sup>4</sup> the N<sub>2</sub> is injected just before the detection mass spectrometer and Kr and Ar are introduced upstream. For the radiative lifetimes the N<sub>2</sub> is injected at different points along the flow tube so that the spatial decay of the vibrationally excited species is monitored. The results of these studies are given in Tables I and II respectively together with the data of other workers.

The vibrational quenching of HCl<sup>+</sup>(v=1) and DCl<sup>+</sup>(v=1) ions in collisions with Ar and Kr atoms at 300K has been measured in order to investigate the effect of changing the vibrational and rotational energy levels while keeping the intermolecular interaction potential unchanged. All quenchings are found to be efficient, P>20%, and the lighter isotope is found to be quenched slightly faster than the heavier one. This is consistent with a dominant role for rotational excitation in the V→T,R process such that the advantage of the larger rotational constant outweighs the disadvantage of the larger vibrational frequency. The same situation had been reported for self-quenching of neutral hydrogen halides and for vibrational predissociation of hydrogen halide dimers and supported theoretically in terms of rotational excitation coupling. The present results weigh strongly against a Landau-Teller type vibrational quenching mechanism for the molecular ions, modified by the existence of the attractive potential.

TABLE I: ION VIBRATIONAL QUENCHING RATE CONSTANT (300K)\*

Ion	Neutral	$10^{12}k_q$ ( $\text{cm}^3\text{s}^{-1}$ )	$k_1/k_q$ Z	$\nu(\text{cm}^{-1})$	$B(\text{cm}^{-1})$
HCl <sup>+</sup> (v=1)	He	<0.3	>1900	2569	9.96
DCl <sup>+</sup> (v=1)	He	<0.2	>2800	1864	5.12
HCl <sup>+</sup> (v=1)	Ar	350	2.0	2569	9.96
DCl <sup>+</sup> (v=1)	Ar	186	3.7	1864	5.12
HCl <sup>+</sup> (v=1)	Kr	660	1.1	2569	9.96
DCl <sup>+</sup> (v=1)	Kr	430	1.7	1864	5.12

TABLE II: VIBRATIONAL LIFETIMES (ms)

Ion	$\nu(\text{cm}^{-1})$	Present	Other work
HCl <sup>+</sup> (v=1)	2569	4.5±0.5	3.0±1 <sup>s</sup> 4.6 <sup>s</sup>
DCl <sup>+</sup> (v=1)	1869	8.0±1	10±2 <sup>s</sup>

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**THE THERMAL ENERGY REACTIONS  $\text{HCl}^+ + \text{SF}_6 \rightarrow \text{SF}_5^+ + \text{HF} + \text{Cl}$   
AND  $\text{HCl}^+ + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{HF} + \text{Cl}$**

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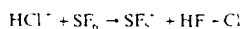
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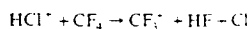
(First received 23 April 1987; in final form 7 July 1987)

**ABSTRACT**

Measurements of the reactions



and



have shown that the first reaction is exothermic and the second nearly thermoneutral. In conjunction with measurements carried out elsewhere, this establishes that  $\text{AE}(\text{SF}_5^+/\text{SF}_6) = 13.98 \pm 0.03$  eV and  $\text{AE}(\text{CF}_3^+/\text{CF}_4) = 14.2 \pm 0.1$  eV. Both of these values are far (over 1 eV) below current literature values obtained from photon and electron impact.

**INTRODUCTION**

In an extension of earlier work at Aberystwyth on the reactions of  $\text{HCl}^+$  ions [1], a program is in progress to measure the vibrational relaxation of  $\text{HCl}^+$  ( $v = 1$ ) and  $\text{DCI}^+$  ( $v = 1$ ) using the same apparatus and applying the monitor ion technique for vibrational state detection that was recently applied to  $\text{O}_2^+$  ( $v$ ) and  $\text{NO}^+$  ( $v$ ) vibrational quenching [2,3]. The number of possible vibrational quenchers of  $\text{HCl}^+$  ( $v$ ) is extremely limited because of the high reactivity of  $\text{HCl}^+$  [1]. It either charge-transfers, proton-transfers, or

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H atom abstracts with almost every molecule. One neutral, which should have been non-reactive according to literature values of ionization energies and proton affinities, is  $\text{SF}_6$ . The parent ion  $\text{SF}_6^+$  is unstable and values of the appearance energy of  $\text{SF}_5^+$  from  $\text{SF}_6$  range from 15.3 to 15.7 eV [4,5]. However, we found that  $\text{HCl}^+$  reacts rapidly to produce  $\text{SF}_5^+$ , implying that these high values of  $\text{AE}(\text{SF}_5^+/\text{SF}_6)$  are in error. The reaction inferred is



because this is the most exothermic possibility. Similarly, we also found the reaction



to occur. For reaction (1), the rate constant,  $1.25 \pm 0.25 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , is close to the Langevin collision rate constant,  $1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , and therefore reaction (1) is exothermic, establishing that  $\text{AE}(\text{SF}_5^+/\text{SF}_6) < 14.17 \text{ eV}$ . Reaction (2) has a rate constant  $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . If the deviation from the Langevin value in this case is entirely due to endothermicity, the reaction could be endothermic by no more than  $kT \ln(k_L/k_2) = 0.06 \text{ eV}$ , therefore  $\text{AE}(\text{CF}_3^+/\text{CF}_4) < 14.23 \text{ eV}$ . That this is likely to be a correct interpretation is established by the increase of  $k_2$  with centre of mass kinetic energy, to  $2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 0.8 eV, suggesting that reaction (2) is very close to thermoneutral. This is further supported by the pseudo-Arrhenius plot ( $k_2$  vs.  $E^{-1} \text{ cm}$ ), the slope of which yields the value  $\Delta E = 0.04 \pm 0.01 \text{ eV}$ .

Babcock and Streit [6] connected the energetics of the  $\text{SF}_6$  and  $\text{CF}_4$  systems by finding the reaction



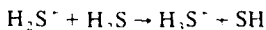
to be 0.17 eV exothermic from equilibrium constant measurements. Reaction (3) is equivalent to  $\text{AE}(\text{CF}_3^+/\text{CF}_4) = \text{AE}(\text{SF}_5^+/\text{SF}_6) + 0.17 \text{ eV}$  and, by combining reactions (2) and (3), one obtains a lower upper limit for  $\text{AE}(\text{SF}_5^+/\text{SF}_6)$  of 14.06 eV.

Babcock and Streit [6] also found



to be fast and therefore exothermic so that  $\text{IE}(\text{SF}_5) > \text{IE}(\text{NH}_3)$ . Values for  $\text{IE}(\text{NH}_3)$  are  $10.154 \pm 0.01 \text{ eV}$  and  $10.162 \pm 0.008 \text{ eV}$  [8].

Babcock and Streit actually reported  $\text{IE}(\text{SF}_5) > 10.43 \text{ eV}$ , based on an observed fast reaction with  $\text{H}_2\text{S}$  ( $\text{IE} = 10.43 \text{ eV}$ ) which they assumed to be charge-transfer, although they did not observe a primary product. They observed  $\text{H}_3\text{S}^+$  as a secondary product which they assumed was due to the known fast reaction

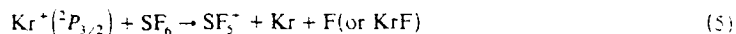




This higher  $IE(SF_3)$  is inconsistent with the  $AE(SF_3^+/SF_6)$  and  $D(SF_3-F)$  and cannot be correct. Richter et al. [9] have re-investigated this reaction in Innsbruck and determined that the reaction of  $SF_3^+$  with  $H_2S$  is not charge-transfer but rather a relatively fast three-body association which simulated a slow binary reaction in the experiments of Babcock and Streit.

Combining a conservative lower limit of 10.14 eV for  $IE(NH_3)$ , and therefore of  $IE(SF_3)$ , with Kiang and Zare's [10] determination of  $D(SF_3-F) = 3.95 \pm 0.14$  eV, one obtains  $AE(SF_3^+/SF_6) = D(SF_3-F) + IE(SF_3) > 13.95$  eV. The recent critical evaluation of Herron [11] gives  $D(SF_3-F) = 4.01 \pm 0.13$  eV, which would give an even larger lower limit of 14.02 eV.

In support of the lower  $AE(SF_3^+/SF_6)$ , Richter et al. [9] have reported the reaction



to be fast and exothermic and we have verified that result in this laboratory. This establishes that  $AE(SF_3^+/SF_6) < IE(Kr) + D(KrF) = 14.0$  eV +  $D(KrF)$ . The dissociation energy of  $KrF$  is very small (0.013 eV [12]) and  $AE(SF_3^+/SF_6) < 14.02$  eV. Also, Shul et al. [13] found the reaction



to be exothermic, implying  $AE(SF_3^+/SF_6) < 14.4$  eV.

The upper and lower limits on  $AE(SF_3^+/SF_6)$  are satisfied by  $AE(SF_3^+/SF_6) = 13.97 \pm 0.04$  eV. The value of  $AE(SF_3^+/SF_6)$  is thus very tightly constrained! Equivalently,  $IE(SF_3) = 10.0 \pm 0.15$  eV and  $\Delta H_f(SF_3^+) = 11.6 \pm 0.7$  kcal mol<sup>-1</sup>, utilizing  $\Delta H_f(SF_6) = -291.7$  kcal mol<sup>-1</sup> [11]. The above constraints show that the upper limits, indeed even the central values, of  $D(SF_3-F)$  are too high [10,11] and imply that  $D(SF_3-F) < 3.9$  eV.

Further, we find that the reaction



does not occur detectably. In view of the similarity of  $CF_4$  and  $SF_6$  ion chemistry, this almost certainly implies that  $AE(CF_3^+/CF_4) < 14.0$  eV, so that reactions (2) and (7) bracket  $AE(CF_3^+/CF_4)$  between 14.06 and 14.24 eV. As discussed above, the energy dependence of reaction (2) supports a value near the upper limit, perhaps  $14.2 \pm 0.1$  eV. All literature values are substantially higher, being typically 15.5 eV [4,5].

This in turn implies a lower  $IE(CF_3)$  than is currently accepted.  $IE(CF_3) = AE(CF_3^+/CF_4) - D(CF_3-F) < 8.64$  eV, where  $D(CF_3-F)$  is taken as 5.6 eV [14]. Kime et al. [15] have recently reviewed the thermochemistry of carbon tetrahalide ions. They give  $IE(CF_3) = 9.3 \pm 0.2$  eV, consistent with earlier values which they tabulate (except for one anomalously high value of 10.8 eV).

Kime et al. [15] also review the literature values of  $D(\text{CF}_3-\text{F})$ ; the lowest value in the literature is 5.03 eV, which is almost surely too low. Of the four other values listed, two are equal to 5.6 eV and two exceed this. It seems inescapable that the present values of  $\text{IE}(\text{CF}_3)$  are substantially too large.

It is apparent that the photoelectron appearance energies for  $\text{SF}_5^+/\text{SF}_6$  and  $\text{CF}_3^+/\text{CF}_4$  measure vertical AEs, which are substantially higher than the adiabatic AEs measured in the ion/molecule reactions. It is characteristic of ion/molecule reactions to yield adiabatic exothermicities by virtue of the intimate contact of sufficient duration to allow molecular geometry relaxation to adiabatic configurations. Ion/molecule reaction studies usually yield reliable adiabatic energy differences. It is, of course, fortuitous, although not unique, for energies to be so tightly constrained by bracketing techniques as they are for  $\text{SF}_5^+/\text{SF}_6$ .

Reactions (1) and (2) are interesting reactions and somewhat unusual in having three product particles. The reactions can be viewed as  $\text{F}^-$  abstraction by  $\text{HCl}^+$  to produce a transient  $\text{ClHF}$  molecule which decays by the most exothermic path to produce  $\text{HF}$  and  $\text{Cl}$ . Since a simple electron transfer from  $\text{SF}_6$  or  $\text{CF}_4$  to  $\text{HCl}^+$  is endothermic by over 1 eV, the  $\text{HF}$  bond formation energy is essential to drive the reaction and one must consider a concerted process to occur in a transient complex. The positive  $\text{H}$  of  $\text{HCl}^+$  approaches the very polarizable  $\text{SF}_6$  ( $\alpha = 4.48 \text{ \AA}^3$ ) and abstracts an  $\text{F}^-$ , falling apart into  $\text{HF} + \text{Cl} + \text{SF}_5^+$ , and similarly for  $\text{CF}_4$ .

The abstraction of  $\text{F}^-$  from  $\text{SF}_6$  by positive ions, producing  $\text{F}$  bonds, is well established from earlier work of Fehsenfeld [16] who found that  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ , and  $\text{CO}^+$  all abstract  $\text{F}^-$  from  $\text{SF}_6$  to form the corresponding neutral fluorides and  $\text{SF}_5^+$ . These reactions are exothermic and occur at near the Langevin rate constant, as in the case of reaction (1). Fehsenfeld found that  $\text{O}_2^+$  and  $\text{NO}^+$  did not react with  $\text{SF}_6$  to produce  $\text{FO}_2$  and  $\text{FNO}$ , respectively, and these reactions are endothermic, even with the new lower value of  $\text{AE}(\text{SF}_5^+/\text{SF}_6)$ .

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VIBRATIONAL QUENCHING OF  $\text{HCl}^+(v=1)$  AND  $\text{DCl}^+(v=1)$  BY Ar AND KrM. TICHY<sup>1</sup>, G. JAVAHERY, N.D. TWIDDY*Department of Physics, University College of Wales, Penglais, Aberystwyth, Dyfed SY23 3BZ, UK*

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The vibrational quenching of  $\text{HCl}^+(v=1)$  and  $\text{DCl}^+(v=1)$  ions in collisions with Ar and Kr atoms at 300 K has been measured in order to investigate the effect of changing the vibrational and rotational energy levels while keeping the intermolecular interaction potential unchanged. All quenchings are found to be efficient,  $P > 20\%$ , and the lighter isotope is found to be quenched slightly faster than the heavier one. This is consistent with a dominant role for rotational excitation in the  $V \rightarrow T, R$  process such that the advantage of the larger rotational constant outweighs the disadvantage of the larger vibrational frequency. The same situation had been reported for self-quenching of neutral hydrogen halides and for vibrational predissociation of hydrogen halide dimers and supported theoretically in terms of rotational excitation coupling. The present results weigh strongly against a Landau-Teller-type vibrational quenching mechanism for the molecular ions, modified by the existence of the attractive potential.

## 1. Introduction

Recently, the first systematic studies of diatomic positive ion vibrational quenching have been carried out, including some information on relative kinetic energy dependence and some limited information on the vibrational state dependence [1-6]. Such measurements have become possible through the use of selected ion flow drift tubes for the production of vibrationally excited ions, their quenching and their detection (by mass), in conjunction with the monitor ion technique (addition of a monitor gas whose reaction with the ion depends on the ion vibrational state). The general pattern that occurs is that quenching is usually rapid. Probabilities exceed  $10^{-3}$  for almost all neutral quenchers except the rare gases and molecular hydrogen. It is also found that ion vi-

brational quenching rate constants generally decrease with relative kinetic energy.

The large quenching rate constants and their negative temperature dependences are a clear indication of the dominant influence of the long-range attractive forces in the quenching process. Most neutral diatomic molecular vibrational quenching ( $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , etc.) is characterised by low efficiency and increasing rate constant with relative kinetic energy. This quenching occurs as a result of the short-range repulsive forces. The "impulsive" energy transfer efficiency increases with collision energy and with the steepness of the interaction potential. The process is well understood in terms of non-adiabatic energy transfer theory and was treated by Landau and Teller [7] and is often referred to as Landau-Teller quenching.

Recently Tanner and Maricq [8] have proposed that efficient molecular ion quenching might be explained by a modified Landau-Teller mechanism. The modification resulting from an attractive well is twofold, an increase in the relative collision energy

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and an increase in the steepness of the repulsive interaction.

In cases where strong attractive forces operate in neutral quenching, a less common situation than for ions which have strong electrostatic attractions, vibrational quenching is also efficient and has a negative temperature dependence. No general theoretical framework is available for the case of quenching controlled by the long-range potential.

The purpose of the present investigation was to isolate the role of vibrational and rotational energy levels while keeping the interaction potential constant by the use of isomers. The only substantial energy level change that can be readily realised for diatomic ions involves hydride ions and their corresponding deuterides. In the present case we have studied  $\text{HCl}^+$  and  $\text{DCl}^+$ , for which the rotational constants change by  $\approx 2$  and the vibrational energy levels by  $\approx \sqrt{2}$ .

One practical problem with  $\text{HCl}^+$  is its extreme reactivity – it reacts with almost every molecule that is tractable for study. Many such reactions were studied earlier in this laboratory [9]. The only suitable quenchers that we have found are the Ar and Kr reported here. According to energies reported in the literature  $\text{SF}_6$  should not have reacted but we found that it did. The value of  $\text{AE}(\text{SF}_6^+/\text{SF}_6)$  in the literature,  $\approx 15.5$  eV, is grossly in error and a value  $13.98 \pm 0.03$  eV has been determined [10].  $\text{CF}_4$  also reacted with  $\text{HCl}^+$  (both  $\text{SF}_6$  and  $\text{CF}_4$  give  $\text{HF} + \text{Cl}^+$  neutral products, and  $\text{SF}_6^+$  and  $\text{CF}_4^+$  ion products) and the literature value of the ionisation energy is again grossly in error, or rather refers to a vertical rather than adiabatic energy. In the present study one has to work with very low fractions of vibrationally excited ions (1–2%). Also the spin-orbit splitting produces two vibrationless states separated by 80 meV,  $^2\Pi_{1/2}$  lying below  $^2\Pi_{3/2}$ , and these are about equally populated in ionization [11]. This produces an interference, as described below. One neutral which does not react exothermically with  $\text{HCl}^+(v=0)$  is  $\text{N}_2$ , whereas  $\text{HCl}^+(v=1) + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{Cl}$  is exothermic and fast [9], so that this proton-transfer reaction provides our monitor of the  $\text{HCl}^+(v>0)$  population.  $\text{N}_2$  is added into the buffered  $\text{HCl}^+$  plus quencher flow just in front of the sampling quadrupole mass spectrometer and the resulting  $\text{N}_2\text{H}^+$  ion signal is proportional to the vi-

brationally excited  $\text{HCl}^+$  population. Hence the decrease in  $\text{N}_2\text{H}^+$  due to quencher (Ar or Kr) addition directly measures the quenching rate constant in the conventional way [1–3]. Only relative ion signal measurements are required.

Unfortunately the  $\text{HCl}^+(^2\Pi_{1/2}, v=0)$  reacts slowly with  $\text{N}_2$  to produce  $\text{N}_2\text{H}^+$ , in spite of its endothermicity, due to the high-energy tail of the 300 K thermal ion and neutral energy distributions. This  $\text{N}_2\text{H}^+$  signal varies much more slowly with Ar or Kr so that it simply provides a  $\text{N}_2\text{H}^+$  background signal to be subtracted, thereby lowering the dynamic range of the measurements and consequently their precision. The  $\text{DCl}^+(^2\Pi_{1/2})$  background contribution to  $\text{N}_2\text{D}^+$  background is less than in the case of  $\text{HCl}^+(^2\Pi_{1/2})$ , about one-half, consistent with the greater endothermicity of the proton transfer to  $\text{N}_2$  because of the lower  $\text{DCl}^+$  zero-point energy.

## 2. Experimental

The apparatus used is essentially that described previously [9] and the monitor ion technique is the same as used here earlier for electronically excited state ion reaction studies [12,13] and elsewhere for vibrational relaxation studies [1–3]. The quenching gases Ar and Kr were BOC research grade and the  $\text{N}_2$  was BOC CP grade. Since the measured quenching rate constants are so large, trace impurities could play no role in the study. The vibrationally excited ions were obtained using a discharge source containing  $\text{HCl}$  ( $\text{DCl}$ ) or  $\text{HCl}$  ( $\text{DCl}$ )-He mixtures.

## 3. Results and discussion

Table I gives the present results and some results for Ar and Kr quenching previously reported for comparison.

The  $\text{HCl}^+(v=1)$  ion represents the highest frequency ion vibration for which collisional relaxation rates have been measured,  $225\text{ cm}^{-1}$  greater than  $\text{NO}^+(v=1)$ . The first striking point about the results is the large efficiency of the quenching (or the small number of collisions,  $Z$ , required for quenching on the average). In the case of Kr, the quenching

Table 1  
Ion vibrational quenching rate constants (300 K)

Ion	Neutral	$10^{12}k_q$ (cm <sup>3</sup> s <sup>-1</sup> )	$k_i/k_q$ Z	$\nu$ (cm <sup>-1</sup> )	$B$ (cm <sup>-1</sup> )	Ref
HCl <sup>+</sup> ( $v=1$ )	He	<0.3	>1900	2569	9.96	
DCI <sup>+</sup> ( $v=1$ )	He	<0.2	>2800	1864	5.12	
HCl <sup>+</sup> ( $v=1$ )	Ar	350	2.0	2569	9.96	
DCI <sup>+</sup> ( $v=1$ )	Ar	186	3.7	1864	5.12	
HCl <sup>+</sup> ( $v=1$ )	Kr	660	1.1	2569	9.96	
DCI <sup>+</sup> ( $v=1$ )	Kr	430	1.7	1864	5.12	
O <sub>2</sub> <sup>+</sup> ( $v=1$ )	He	<0.002	>3×10 <sup>7</sup>	1872	1.69	[1]
O <sub>2</sub> <sup>+</sup> ( $v=1$ )	Ar	1.0	710	1872	1.69	[1]
O <sub>2</sub> <sup>+</sup> ( $v=2$ )	Ar	2.5	280	1840	1.69	[1]
O <sub>2</sub> <sup>+</sup> ( $v=1$ )	Kr	11	69	1872	1.69	[1]
O <sub>2</sub> <sup>+</sup> ( $v=2$ )	Kr	17	45	1840	1.69	[1]
NO <sup>+</sup> ( $v>0$ )	He	<0.1	>5600	2344	2.00	[3]
NO <sup>+</sup> ( $v>0$ )	Ar	<1	>710	2344	2.00	[3]
NO <sup>+</sup> ( $v>0$ )	Kr	<0.08	>9000	2344	2.00	[14]

of HCl<sup>+</sup> ( $v=1$ ) is  $\approx 60$  times more efficient than the quenching of O<sub>2</sub><sup>+</sup> ( $v=1$ ) and over 8000 times more efficient than NO<sup>+</sup> ( $v>0$ ) quenching.

A second point to be noted is the similarity between the Ar and Kr quenching rates, they differ by only  $\approx 2$  with Kr being more efficient.

By contrast Kr quenches O<sub>2</sub><sup>+</sup> ( $v=1$ ) an order of magnitude more efficiently than does Ar and the ratio is almost as large (6.8) for O<sub>2</sub><sup>+</sup> ( $v=2$ ). This has been attributed to the deeper attractive well for ions with Kr due to the larger Kr polarisability (2.48 Å<sup>3</sup> compared to 1.64 Å<sup>3</sup> for Ar) as well as the lower ionisation energy of Kr (14.0 eV) compared to Ar (15.7 eV). It has recently been shown that the charge-transfer contribution to the attractive potential is significant: being as much as 40% for the attractive potential for O<sub>2</sub><sup>+</sup> and Kr, 36% for NO<sup>+</sup> and Kr, 38% for O<sub>2</sub><sup>+</sup> and Ar and 37% for NO<sup>+</sup> and Ar [13].

Similar arguments would apply to the HCl<sup>+</sup> and DCI<sup>+</sup> ions, i.e. the electrostatic and charge-transfer interactions would both be greater for Kr than for Ar and, in addition, the proton affinities of Kr (101.6 kcal mol<sup>-1</sup>) and Cl (123.0 kcal mol<sup>-1</sup>) are closer together than are Kr and Ar (88.6 kcal mol<sup>-1</sup>) so that any tendency for stability by non-resonant proton transfer would favour the Kr over the Ar. The HCl<sup>+</sup> ( $v=1$ ) quenching by Kr occurs on virtually every collision, so one cannot safely deduce dynamical properties of the collision from this. A simple statistical, phase space argument in a relatively long-

lived complex is a satisfactory interpretation of this result.

The third point to be noted is the slight preference for HCl<sup>+</sup> ( $v=1$ ) quenching over DCI<sup>+</sup> ( $v=1$ ) quenching for both Ar and Kr. This has immediate significance in that it clearly weighs against a Landau-Teller-type process in which the adiabatic V→T energy transfer is driven by the impulsive collision with the repulsive wall. The critical "adiabatic" parameter [15]  $\xi = av/v$  is simply the collision lifetime,  $a/v$  (where  $a$  is a characteristic distance, the repulsive force range parameter, and  $v$  is the relative velocity), divided by the vibrational period  $T = 1/\nu$ , and the probability of quenching is [15-17]  $P \sim \exp(-\xi)$ . Reducing  $\nu$  then drastically (exponentially) increases  $P$  in this Landau-Teller-type relaxation. This Landau-Teller failure is consistent with the previous finding from relative O<sub>2</sub><sup>+</sup> ( $v$ ) and NO<sup>+</sup> ( $v$ ) quenching rate constants with common neutral quenchers that no energy gap (or momentum gap) principle appears to be operative in ion quenching [18].

We believe that both the efficiencies and the isotope effects in the HCl<sup>+</sup>/DCI<sup>+</sup> quenching are a consequence of the importance of rotational product excitation in the V→T, R process and the distinguishing significant characteristic of the hydride ions is their large rotational constant and the marked anisotropy of the potential due to the large dipole moments of the halide ions. The rotational excitation

can be either in the ion as here or in the neutral (or both) for the case of molecular neutrals. The more efficient quenching of  $O_2^+(v)$  by  $H_2$  than by  $D_2$  ( $v \approx 4$ ) has been attributed to the larger  $H_2$  rotational constant [18].

The same situation occurs for neutral hydrogen chloride vibrational self-quenching. In this case the substantial attractive potential is a consequence of hydrogen bonding. The  $HCl(v=1)$  quenching by  $HCl$  is about twice as fast as  $DCl(v=1)$  quenching by  $DCl$  [19]. This has been explained by Shin [20] as a rotational effect.

Similarly, the vibrational predissociation of  $(HF)_2$  dimer is faster than  $(DF)_2$  dimer [21], and this has also been explained as a rotational effect by means of close coupling calculations [22].

There appears to be little, if any, inherent difference in ion and neutral vibrational relaxation when these have comparable interaction potentials. Of course, relatively large attractions are the general rule for ions due to the electrostatic attraction but are more the exception for (small) neutrals.

The significant role of rotational excitation is intimately related to the importance of anisotropy of the interaction potential. This has been shown already by Osborn and Smith [23] from trajectory calculations for model neutral quenching situations with significant attractive forces. It has also been shown to be important by Tost et al. [24] in trajectory calculations for the quenching of  $O_2^+(v)$  by Kr, the only ion quenching case so far that has been measured as a function of relative energy through the region of a minimum in rate constant. The minimum occurring broadly in the energy region of the potential well depth ( $\approx 0.33$  eV) demonstrates the predominance of the attractive forces at energies much below the well depth and the repulsive forces at energies large compared to the well depth [1].

The importance of anisotropy is also an inference from the analysis of Gislason and Ferguson [25] relating vibrational quenching to interaction potentials for the available  $O_2^+(v)$  and  $NO^+(v)$  quenching data. It is suggested there that the key element of the anisotropy in the case of non-polar neutral quenchers may be due to the short-range charge-transfer (or wavefunction overlap) interaction in some cases rather than to the anisotropy of the long-range potential. This proposition is supported qualitatively

by the correlation between quenching rate constants and the calculated charge-transfer interaction for the  $O_2^+(v)$  and  $NO^+(v)$  quenching data that are available [25].

The fact that no significant decrease in the background  $N_2H^+$  signal, arising from  $HCl^+(^2\Pi_{1/2})$  reaction with  $N_2$ , with Ar and Kr addition implies at most a very slow  $HCl^+(^2\Pi_{1/2}) + HCl^+(^2\Pi_{1/2})$  quenching by Ar or Kr, less than  $10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

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The application of a selected ion flow drift tube to the  
determination of proton affinity differences.

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Abstract

The forward and reverse rate constants for nine proton transfer reactions have been measured as a function of relative kinetic energy using a selected ion flow drift tube (SIFDT). In all but two cases van't Hoff plots of the equilibrium constant against reciprocal centre of mass collision energy were linear and values of the enthalpy and entropy changes were obtained from slope and intercept respectively. Since  $\Delta H$  is a measure of the difference between the proton affinities of the two neutral species, the data can be used to provide a proton affinity difference ladder. This ladder agrees extremely well with the established proton affinity scale. The experimental values of entropy change agree well with values calculated from the entropies of the individual ions and neutrals. The agreements of the  $\Delta H$ 's and  $\Delta S$ 's so determined establishes the validity, and utility, of a SIFDT apparatus for proton affinity studies, reversing the previously held view which was based on FDT measurements involving  $N_2OH^+$ . In the present study two  $N_2OH^+$  measurements gave non-linear Arrhenius and van't Hoff plots, and had to be rejected, in agreement with the earlier work. Some speculations of why drift tube measurements lead to reliable thermodynamic data, in spite of the lack of thermodynamic equilibrium between internal and translational modes, are presented.

### Introduction

Experimental determinations of the forward and backward rate constants for proton transfer reactions of the general type



have been widely used,<sup>1,2,3</sup> to obtain data on proton affinities. If the equilibrium constant  $K = k_f/k_r$  is measured as a function of temperature then from a van't Hoff plot of  $\log K$  versus  $1/T$  the enthalpy and entropy changes,  $\Delta H$  and  $\Delta S$ , can be determined from the slope and the intercept on the ordinate respectively. The value of  $\Delta H$  is equal to the difference of the proton affinities of X and Y and  $\Delta S$  is related to the ion structures. Often,  $K$  is measured only at 300K and  $\Delta S$  is determined from known or theoretical entropies.

Recently in connection with unrelated studies, we made the chance observation that the reactions of  $\text{HBr}^+$  with both  $\text{CO}_2$  and  $\text{CH}_4$  are endoergic<sup>4</sup>. Both reactions are proton transfer reactions so that it was immediately evident that the proton affinities of  $\text{CO}_2$  and  $\text{CH}_4$  are less than the proton affinity of Br. This indicated that the NBS tabulated value<sup>5</sup> for  $\text{PA}(\text{CH}_4)$  was slightly too high (in agreement with a recent high level theoretical calculation<sup>6</sup>) and particularly that a recently proposed increase<sup>7</sup> in proton affinities in the 130 - 140 kcalmol<sup>-1</sup> range is clearly incorrect.

The problem in establishing an absolute proton affinity scale lies in determining one or more fixed points to anchor the relative scales that have been deduced by van't Hoff plots as described above. Since the proton affinity of Br is known with spectroscopic precision<sup>a</sup> from the dissociation energy of HBr<sup>+</sup>, this suggested the possibility of obtaining an improved PA scale anchored to PA(Br).

In order to establish PA's relative to Br, and to each other, proton transfer reaction rate constants were measured in a temperature variable SIFT at Birmingham<sup>a</sup>. Values for PA's of CO, Br<sub>2</sub>, HBr, N<sub>2</sub>O, HCl, CH<sub>4</sub> and CO<sub>2</sub> were determined relative to Br, with what is believed to be an improved accuracy, conservatively estimated to be better than  $\pm 1$  kcal mol<sup>-1</sup>. For six common species the new scale has average deviations from the NBS scale of 1.7 kcal mol<sup>-1</sup>, with a maximum deviation of 2.8 kcal mol<sup>-1</sup> (for HBr). In most cases the new values of PA are slightly smaller than the NBS values, but not in every case.

In the course of these studies we have learned, to our surprise, that reliable PA differences can be obtained from "van't Hoff" plots of rate constant vs reciprocal average centre of mass kinetic energies i.e. from SIFDT measurements. This has important practical implications because the wide KE range ( $\sim 1$  eV) far exceeds the maximum temperature variation possible ( $< 900^\circ\text{K} \approx 0.1$  eV), allowing much larger P.A. differences to be spanned for a single reaction. Also elevated temperature flow tubes are notoriously difficult to operate and maintain.

The applicability of SIFDT'S to thermochemical problems is quite surprising since the internal degrees of freedom are not equilibrated with the translation kinetic energy. The neutral

reactants maintain 300K rotational and vibrational temperatures, the ions attain rotational equilibrium with the relative KE in a few collisions<sup>10</sup>, but the ion vibrations do not<sup>11</sup>, at least for low KE's and the relatively small number of collisions of the ions with the buffer in typical SIFT experiments.

We were reinforced in this expectation, or perhaps more properly, led to this expectation by experience with the forward and reverse proton transfers between  $N_2O$  and  $CO$ , for which linear van't Hoff plots vs  $T^{-1}$  are obtained<sup>2</sup>, yielding reliable proton affinity differences and entropy changes in reaction, whereas  $KE^{-1}$  van't Hoff plots were markedly non linear. The Arrhenius plots for both forward and reverse reactions i.e.

$k = A \exp(-\Delta E/RT)$  were also linear in this case, whereas the "Arrhenius" plot for  $N_2OH^+$  reaction with  $CO$  as a function of  $KE^{-1}$  was non-linear. We still find non-linear Arrhenius plots for  $N_2OH^+$  reacting with  $CO$  and also with  $HBr$  but we find linear plots for 14 other reactions and it appears that the non-linearity is, at least to some extent, a problem peculiar to  $N_2OH^+$ , perhaps related to the existence of two isomeric forms lying very close in energy.

The present paper shows that reliable PA differences and entropy changes are obtained from  $KE^{-1}$  plots by comparison of these measurements with available data on well understood reactions.

In the case of  $N_2OH^+$ , and presumably for other ions as yet unmeasured, for which the non-thermodynamic equilibrium is important, linear plots are not obtained and one would not

attempt to deduce  $\Delta H$  and  $\Delta S$ . It seems unlikely therefore that one would be lead to errors when the SIFDT technique does fail, as in the case of  $N_2OH^+$ .

The Lindinger et al<sup>2</sup> paper was a detailed study of flow-drift tubes using various carrier gases (He,  $N_2$ , Ar) and showed that the proton transfer reactions of  $N_2OH^+$  were very dependent upon the vibrational excitation of the ions and that a helium buffer was less effective in producing vibrational excitation than a heavier buffer. This is now well understood from the vibrational quenching study of vibrationally excited ions that have been subsequently obtained<sup>11</sup>.

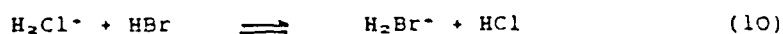
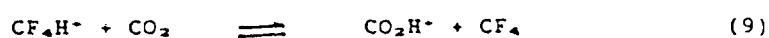
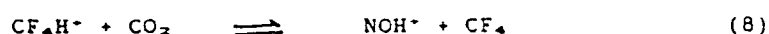
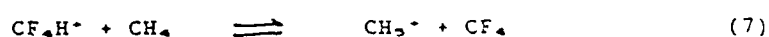
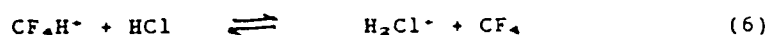
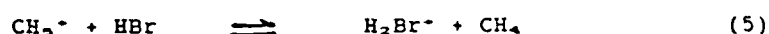
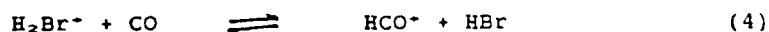
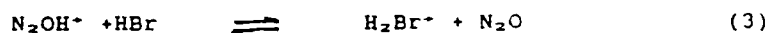
#### Experimental

The measurements were made in the Aberystwyth selected-ion flow-drift tube apparatus which has been described previously<sup>12</sup>. The ions studied  $N_2OH^+$ ,  $H_2Br^+$ ,  $HCO^+$ ,  $H_2Cl^+$ ,  $CF_3H^+$ ,  $NOH^+$ ,  $CO-H^+$  and  $CH_3^+$  were generated in a high pressure ion source using  $HCl$ ,  $HBr$ ,  $CO_2$ ,  $CH_4$ , or  $CO$  mixed with  $H_2$ .

The neutral reactant was added further downstream and the centre of mass collision energy  $E_{cm}$  was varied by varying the axial drift tube electric field. In such an apparatus the forward reaction rate constant can be determined as a function of  $E_{cm}$ . The corresponding data for the reverse reaction is obtained straightforwardly in a second experiment injecting the appropriate ion and neutral species.

### Results and Discussion

The nine reactions studied were:-



The van't Hoff plots for these nine reactions are shown in figures 1 and 2 together with the data of Lindinger et al<sup>2</sup> for reaction(2). It is evident that there is excellent agreement between Lindinger et al and the present measurements so that the non-linearity of the van't Hoff plot for (2) is not in question. For reaction(3) the non-linearity is even more pronounced and it would again be quite impossible to determine either  $\Delta H$  or  $\Delta S$ .

Both the above reactions involve the ion  $\text{N}_2\text{OH}^+$ .

For the remaining seven reactions (4) to (10), in which  $\text{N}_2\text{OH}^+$  is not involved, the pattern is entirely different. These give linear van't Hoff plots yielding values of  $\Delta H$  and  $\Delta S$  listed in Table 1. Such plots can be represented by the expression

$$\ln K = \Delta S/R - \Delta H/RT = \Delta S/R - 3 \Delta H/2E_{\text{cm}} \text{ where } E_{\text{cm}} = \frac{3}{2} RT$$

This will only yield linear plots if  $\Delta H$  and  $\Delta S$  do not change significantly over the energy range of the investigation.

Presumably a significant variation of  $\Delta H$  and  $\Delta S$  with  $E_{\text{em}}$  would result in a non-linear van't Hoff plot. If significant vibrational excitation of the ions by the strong applied field occurred this would change the value of  $\Delta H$  as the  $E_{\text{em}}$  is varied, producing non-linearity. Therefore it can be concluded that in the case of the 7 good van't Hoff plots these effects are insignificant. This implies that the value of  $\Delta S$  obtained from the intercept should be in good agreement with that calculated from the entropies of the ions and molecules involved in these reactions and this should be a sensitive test of the above conclusions. The data so obtained is given in Table 1.

The good agreement between the  $\Delta H$ 's obtained and the established values and the good agreement between calculated  $\Delta S$ 's and the values obtained from the intercepts establishes the validity of the SIFDT apparatus for such measurements.

The average deviation in  $\Delta H$  between the present measurements and the proton affinities of ref.9 is  $0.36 \text{ kcal mol}^{-1}$ , well within the uncertainty of any present proton affinity scale including that of ref.9. The average deviation in  $\Delta S$  determined from the intercepts of Fig.1 and calculated values is 1.5 entropy units. This would correspond to  $T\Delta S = 0.45 \text{ kcal mol}^{-1}$  at 300K and is generally within uncertainties of the entropies of the ions involved.



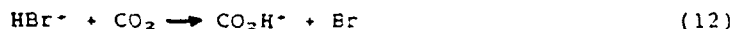
The only ions of Table I whose entropies are known are  $\text{HCO}_2^-$  ( $55.6 \pm 0.8$ ),  $\text{CH}_3^-$  ( $50.4 \pm 0.5$ ) and  $\text{HCO}^-$  ( $48.0 \pm 0.2$ ) from Bolme et al<sup>3</sup>. The entropy of  $\text{H}_2\text{Cl}^-$  is assumed equal to that of the isoelectronic  $\text{H}_2\text{S}$ , 49.2eu, that of  $\text{HBr}$  equal to that of  $\text{H}_2\text{Se}$  = 54.2eu and  $S(\text{HNO}^-)$  is taken equal to  $S(\text{HCO})$  = 53.7eu. The one undetermined entropy  $S(\text{CF}_4\text{H}^-)$  is determined as the best fit to equations 6,7,8 and 9 so that only 6 of the 7 entropy fits are independent. The values of  $S(\text{CF}_4\text{H}^-)$  deduced is 66.6eu. This gives a protonation of  $\text{CF}_4$  of 4.1 eu, consistent with the usual range of values found e.g.  $\text{CH}_4$  (5.9),  $\text{HCl}$  (4.6),  $\text{CO}_2$  (4.5),  $\text{NO}$  (3.4) and  $\text{CO}$  (0.8) and  $\text{HBr}$  (4.9). The quality of these or probably any other such available ion entropies are not sufficiently good to justify serious structural consideration.

One qualification must be made concerning our comparisons of  $\Delta(\text{PA})$  values with those of ref.9, namely, temperature variable measurements involving  $\text{CF}_4$  and  $\text{NO}$  proton transfer reactions were not carried out in Birmingham and the values of  $\text{PA}(\text{CF}_4)$  and  $\text{PA}(\text{NO})$  in ref.9 are those deduced from the present SIFDT studies. One could simply reduce the 7 cases of agreement by two, leaving 5 cases of agreement to support the present justification for the use of the SIFDT. The situation is somewhat better than this however, for two reasons. It is

obvious from the occurrence of very fast proton transfer between  $\text{CF}_4$  and NO in both directions ( $>10^{-10}\text{cm}^3\text{s}^{-1}$ ) that their PA's are closely the same, i.e. the uncertainty in their PA difference is clearly less than  $0.5\text{ kcal mol}^{-1}$  independent of any knowledge of T or KE dependence. Secondly the PA's of both  $\text{CF}_4$  and NO agree within better than  $1\text{ kcal mol}^{-1}$  with values previously determined<sup>2</sup>, although the new values<sup>2</sup> are certainly more precise.

There is strong evidence that the non-linearity of the van't Hoff plots for reactions (2) and (3) is related to the  $\text{N}_2\text{OH}^+$  ion. A linear van't Hoff plot implies that there must be linear Arrhenius plots associated with both  $k_{\text{f}}$  and  $k_{\text{r}}$  for each reaction. For the nine reverse reactions studied we have 18 Arrhenius plots, 16 of which are linear and 2 are markedly non-linear. The last two are for the reactions  $\text{N}_2\text{OH}^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{N}_2\text{O}$  and  $\text{N}_2\text{OH}^+ + \text{HBr} \rightarrow \text{H}_2\text{Br}^+ + \text{N}_2\text{O}$  and are illustrated in Figure 3. It is these two Arrhenius plots which when combined with the two linear Arrhenius plots for the appropriate reverse reactions produce the two non-linear van't Hoff plots of Figure 2 that are associated with reactions (2) and (3).

To supplement the above data there are two other reactions which have been studied previously, but which were measured in one direction only. These are



so that only Arrhenius plots for the reverse direction are available, but these can be used to establish an approximate link to Br although this link is less accurate since the slope of the forward reaction Arrhenius plots are not known. The uncertainty in the estimates of the small temperature dependences of the fast exothermic reaction is the origin of the uncertainty in the present PA scale<sup>o</sup>. The Arrhenius plots give  $\Delta H = 0.6$  and  $3.0 \text{ kcal mol}^{-1}$  respectively. The value  $3.0 \text{ kcal mol}^{-1}$  for (12) agrees well with the value deduced from the T dependence of (12), to which the PA scale is tied<sup>o</sup>. The Arrhenius plot for  $\text{HBr}^+ + \text{CH}_4$  is shown in Fig.3.

Let us consider briefly, and speculatively, why SIFDT studies of proton transfer reactions may yield linear Arrhenius rate constants, and therefore linear van't Hoff equilibrium constant plots, yielding correct values of  $\Delta H$  and  $\Delta S$ , as we have established for the present several cases.

What is clear is that rotations and vibrations of the neutral reactants are not excited in the SIFDT, i.e. they remain in a thermal (300K) distribution. It is also likely that the ions are rotationally equilibrated with the relative KE, consistent with

theoretical prediction<sup>13</sup> and experiment<sup>10</sup> in the case of atomic buffer gases, as for He in the present case. The major uncertainty concerns ion vibrational excitation. It is uncertain to what extent the ions are vibrationally excited in the He buffer gas. The presumptive evidence, from the validity of the KE "van't Hoff" plots is that rotations and vibrations play no role. As a general observation, it has been commonly observed that exoergic proton transfer occurs on nearly every collision for small molecules such as considered here. This suggests that the sole criterion is energy and not the rotational and vibrational states involved except as they contribute to making an endoergic reaction exoergic.

With regard to rotation, one does not expect a significant rotational effect in such reactions, in part because the rotational quanta are so small and one expects small  $\Delta J$  change propensities, a sort of angular momentum conservation. Recently Viggiano et al<sup>14</sup> have made the first specific rotational dependence studies for ion molecule reactions and find the effects to be small.

With regard to vibration, He is an extremely poor vibrational exciter, especially for the high frequency H stretching modes and most of the experiments are carried out at energies below the H stretching energy threshold. The linearity of the plots of Fig.1. clearly indicate that there is not an onset of vibrational excitation with a consequent sharp change of reactivity. The extent of vibrational excitation of the lower frequency bending modes is unknown, and quite possibly significant but apparently does not yield an effect.

The proton transfer reaction



known to be proton transfer and not H atom transfer as a result presumably of the much weaker  $\text{H}_2^+$  bond, has been studied as a function of  $v$  and  $\text{KE}^{15}$ . The results are quite consistent with the present deduction of a weak vibrational effect. The cross section decreases very slightly with  $v$  at low  $E_{\text{cm}} = 0.11\text{eV}$  and very much less at  $E_{\text{cm}} = 0.46\text{eV}$  and not at all at  $E_{\text{cm}} = 0.93\text{eV}$ . At low centre of mass  $\text{KE}$ 's, where there is a slight change in rate constant with  $v$ , there would be no vibrational excitation in a drift tube (it would be energetically impossible) and at high  $\text{KE}$  where there might be vibrational excitation there is no vibrational effect on rate constant. One does not know how generalized this situation is but it accords well with present findings.

It is known that vibrational energy can effectively drive an otherwise endoergic reaction, e.g. the slow endoergic  $\text{HCl}^+ (v=0) + \text{N}_2 \longrightarrow \text{N}_2\text{H}^+ + \text{Cl}$  becomes very fast for  $v = 1^{16}$ .

With regard to the very non linear behaviour of the  $\text{N}_2\text{OH}^+$  reactions, shown in Fig.2, we might suppose that this is a consequence of the occurrence of two isomeric forms,  $\text{N}_2\text{OH}^+$  and  $\text{N}_2\text{OH}^+$ , separated by only  $6 \pm 1.3 \text{ kcal mol}^{-1}^{17,18}$ . There are also two isomeric forms of  $\text{HCO}^+$  and  $\text{HNO}^+$  but the energy separations are much larger, larger than the  $\text{KE}$ 's involved in the drift tube. The two forms are known to be produced in the SIFDT source and to have different reactivities<sup>19</sup>. Since the van't

Hoff temperature plots were well behaved<sup>2,9</sup>, one may ask why the KE plots were different. One possibility is that the different ion sources produced different distributions of isomers. Possibly in the higher pressure variable temperature flow tube ion source the ions were relaxed to the lowest energy form. Alternatively, perhaps the higher energy collisions in the SIFDT, where the non-linearity becomes severe, induce transitions between the two isomers.

#### Conclusions

The use of SIFDT's, in which rate constants are measured as a function of relative ion-neutral kinetic energy has been found to yield linear Arrhenius plots for a number of forward and reverse proton transfer reactions and hence linear van't Hoff plots from their ratio. The values of  $\Delta H$  and  $\Delta S$  are found to be in excellent agreement with the established values for these reactions. The only deviations from linearity observed involved protonated nitrous oxide. This may be related to the existence of two closely lying  $N_2OH^+$  isomers, only 6 kcal mol<sup>-1</sup> apart in energy. It thus appears that KE van't Hoff plots are often linear and when they are they yield valid thermochemical data. When such plots are not linear, for whatever reason, for example as a consequence of the inherent non-thermodynamic equilibrium between vibrations and translations in a drift tube, this will not lead to error since the non-linearity will preclude such use. This expanded role for flowdrift tubes is potentially very useful because of the extremely limited capability for making temperature variable ion-molecule reaction rate constant measurements

ACKNOWLEDGEMENT.

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Table I

Values of  $\Delta H$  and  $\Delta S$  from  $\ln K_{eq} = \Delta S/R - 3\Delta H/2E_{eq}$

(Text No).	Reaction	$-\Delta H$ kcalmol <sup>-1</sup>	$-\Delta H^\circ$ kcalmol <sup>-1</sup>	$\Delta S$ eu	$\Delta S(\text{calc})$
4.	$H_2Br^+ + CO = HCO^+ + HBr$	2.0	2.6	1.4	-4.1
5.	$CH_3^+ + HBr = H_2Br^+ + CH_4$	9.1	8.8	-1.7	-1.0
10.	$H_2Cl^+ + HBr = H_2Br^+ + HCl$	6.0	5.8	+0.6	+0.3
6.	$CF_4H^+ + HCl = H_2Cl^+ + CF_4$	7.0	6.5	-0.2	+0.5
7.	$CF_4H^+ + CH_4 = CH_3^+ + CF_4$	4.0	3.5	-1.7	-1.8
8.	$CF_4H^+ + NO = HNO^+ + CF_4$	0.6	0.5	-3.7	-0.7
9.	$CF_4H^+ + CO_2 = HCO_2^+ + CF_4$	1.7	2.0	+0.4	+0.4

Entropies of neutrals from Benson (Ref. 20)

Entropies of  $HCO^+$ ,  $CO_2H^+$  and  $CH_3^+$  from Bohme et al (ref. 3)

$S(H_2Cl^+)$  assumed =  $S(H_2S) = 49.2$  eu

$S(HNO^+)$  " =  $S(HCO) = 53.7$  eu

$S(H_2Br^+)$  " =  $S(H_2Se) = 52.4$  eu

$S(CF_4H^+)$  " = 6.7, 8 and 9. = 66.6 eu

best fit to equations

Figure Captions

- Fig.1 Showing van't Hoff plots for reactions (4) to (10)
- Fig.2 Showing non-linear van't Hoff plots obtained for reactions (2) and (3). Reaction (2): present,  $+$  reference 2,  $\bullet$ , Reactions (3): present,  $\blacksquare$ .
- Fig.3 Showing Arrhenius plots for reactions (2) and (3).  
 Reaction (2) : forward  $\blacktriangle$ , reverse  $\triangle$ .  
 Reaction (3) : forward  $\bullet$ , reverse  $\circ$ . The Arrhenius plot for reaction (11) is also shown plotted as  $\blacksquare$ .

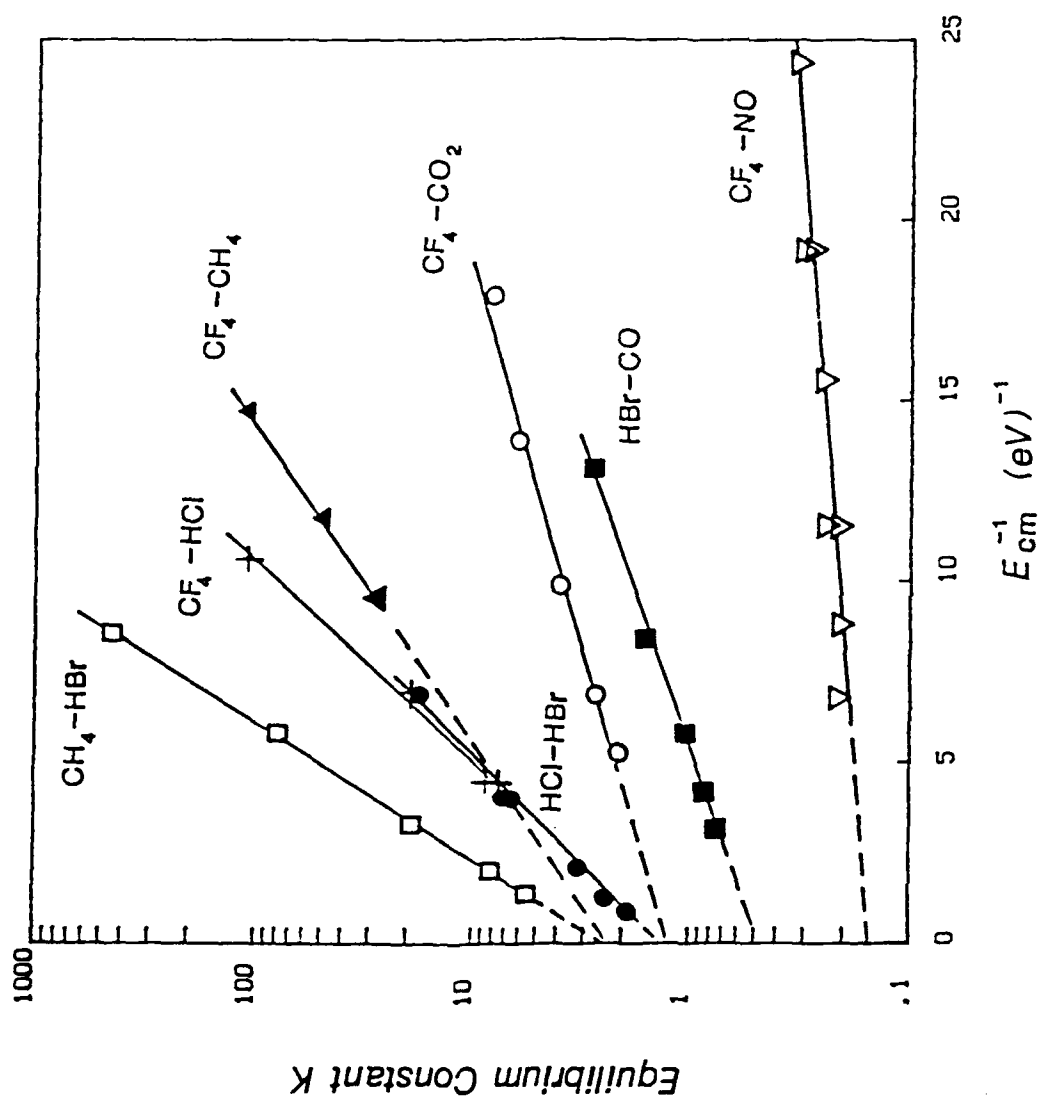


Fig 1

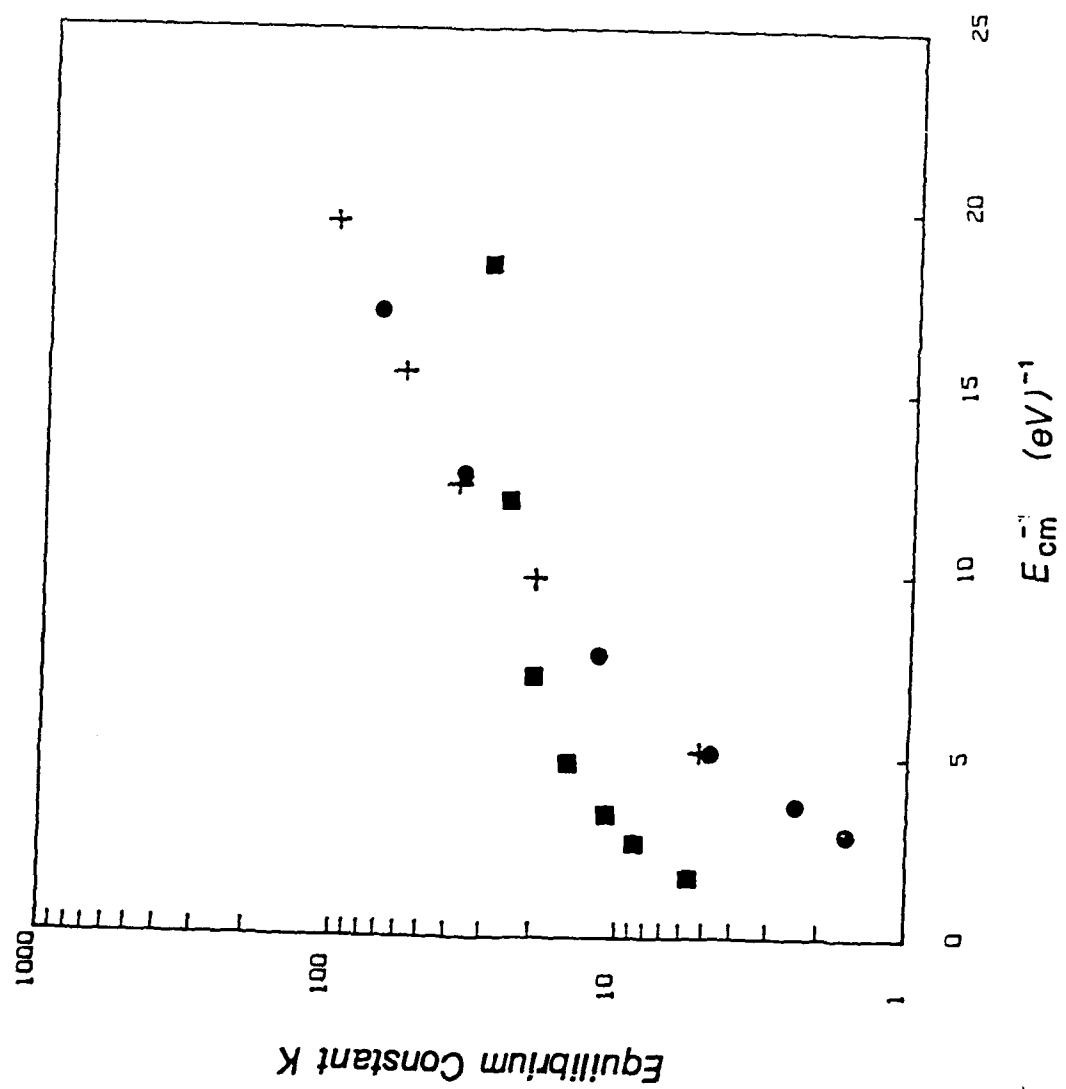
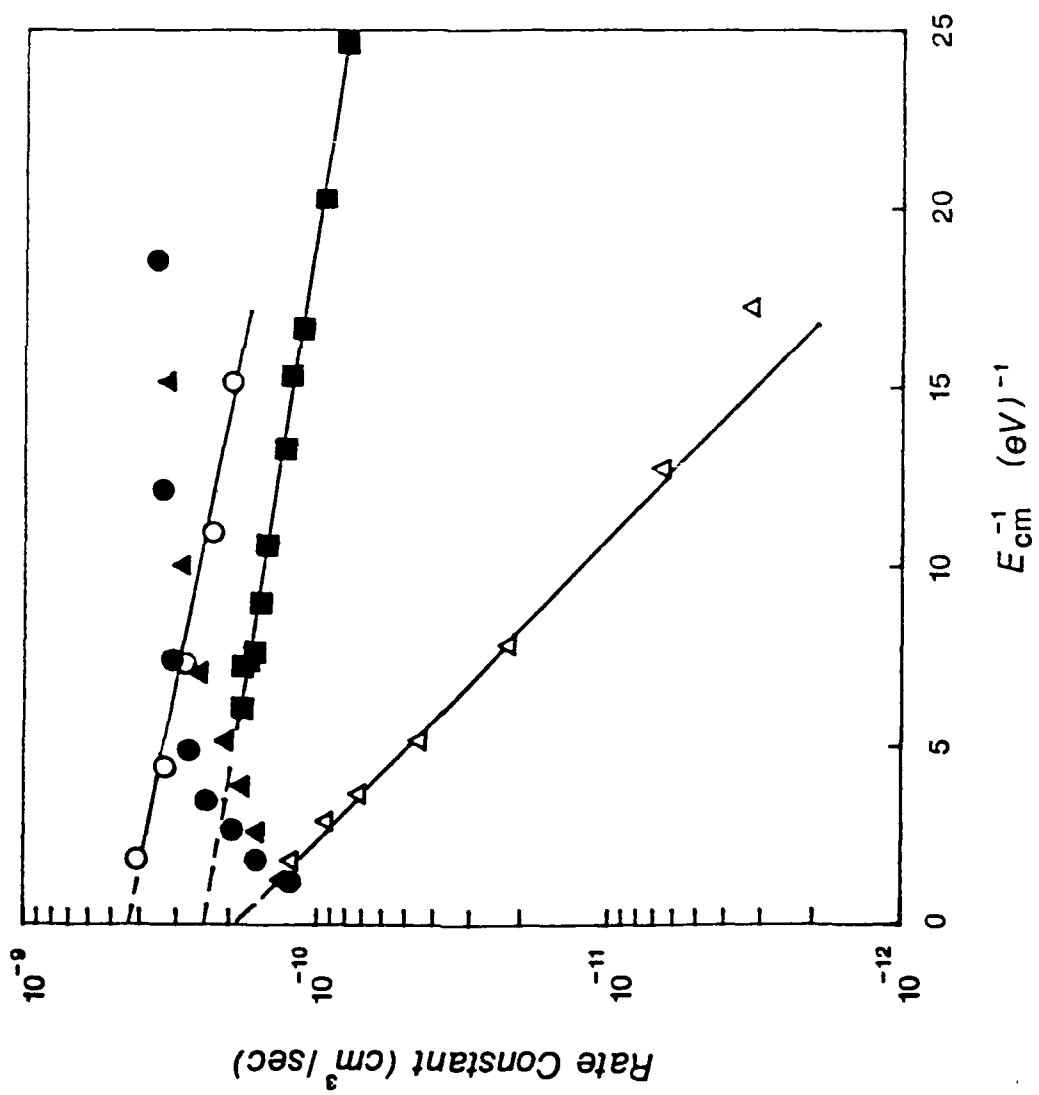


Fig 2



ION CHEMISTRY OF  $\text{HCl}^+$  AND  $\text{HBr}^+$  AND VIBRATIONAL QUENCHING  
RATE CONSTANTS OF  $\text{HCl}^+(\nu = 1)$  AND  $\text{DCI}^+(\nu = 1)$ .

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A study of vibrational quenching of  $\text{HCl}^+$  and  $\text{DCI}^+$  in collisions with neutrals has been carried out in order to change the ion rotational and vibrational energy levels while maintaining the interaction potential constant. This provides a critical test of energy transfer models. Reactions of  $\text{HCl}^+$  with  $\text{SF}_6$  and  $\text{CF}_4$  have been observed with major implications for the thermochemistry of these molecules. Proton Transfer reactions of  $\text{HBr}^+$  may resolve the current controversy over the proton affinity scale in the  $\sim 120\text{--}150\text{ kcal mol}^{-1}$  range.

#### EXPERIMENTAL

The Flowing Afterglow system is that used for earlier studies of  $\text{HCl}^+$  chemistry<sup>1</sup>. Vibrationally excited  $\text{HCl}^+(\text{DCI}^+)$  ions are detected by their fast exothermic proton transfer to  $\text{N}_2$ , which is endothermic (and slow) for ground state  $\text{HCl}^+$  ions<sup>1</sup>. The experiments were complicated, relative to earlier studies of  $\text{O}_2^{+2}$  and  $\text{NO}^{+3}$  vibrational quenching due to several factors: (i) vibrational excitation in electron ionization is weak due to nearly vertical FC factors, (ii) substantial ion vibration depletion occurs by fast IR emission, (iii) the upper  $^2\pi_{1/2}$  fine structure level gives a slow endothermic reaction with  $\text{N}_2$  at 300 K which leads to an interfering background, and (iv) the extreme reactivity of  $\text{HCl}^+$  sharply limits the possible quenchers that can be studied.

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# VIBRATIONAL QUENCHING

The only tractable quenchers that we discovered were Ar and Kr, other species reacted with  $\text{HCl}^+$ . The results obtained with Ar and Kr are given in Table I. He was the buffer gas and did not measurably quench. Z is the number of collisions required on average, to quench.

TABLE I

Ion	$\nu(\text{cm}^{-1})$	$B(\text{cm}^{-1})$	Quencher	$k_q(\text{cm}^3\text{s}^{-1})$	Z
$\text{HCl}^+(\nu = 1)$	2569	9.96	Ar	$3.5(-10)$	2.0
"			Kr	$6.6(-10)$	1.1
"			He	$< 1(-12)$	$> 10^3$
$\text{DCl}^+(\nu = 1)$	1869	5.12	Ar	$1.9(-10)$	3.7
"			Kr	$4.3(-10)$	1.7
"			He	$< 1(-12)$	$> 10^3$

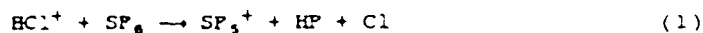
The results of Table I are striking in the large magnitude of the rate constants and the fact that  $\text{HCl}^+$  is quenched slightly faster than  $\text{DCl}^+$ . The values of  $k_q$  are orders of magnitude larger than those of  $\text{O}_2^+$  and  $\text{NO}^+$  by Ar and Kr<sup>2,3</sup>. The quenching of  $\text{HCl}^+$  by Kr is over 700 times faster than  $\text{NO}^+$ .<sup>4</sup>

These observations support a dominant role for rotational excitation in vibrational quenching for systems with strong long range attractive forces. The large rotational constants lead to large  $k_q$ 's and the larger rotational constant of  $\text{HCl}^+$  outweighs the disadvantage of its higher vibrational frequency which necessitates a larger  $V \rightarrow T,R$  energy conversion. This conflicts with recent attempts to explain ion vibrational relaxation by a Landau Teller mechanism<sup>5</sup>.

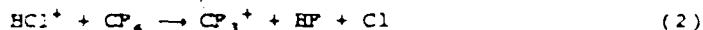
It is consistent with earlier recognition of the dominant role of rotational excitation in neutral HCl self vibrational relaxation<sup>6</sup> and in HP dimer vibrational predissociation<sup>7</sup>. We suggest that ion vibrational relaxation occurs as vibrational predissociation in the transient ion-quencher collision system resulting from the long range forces. This is an extension of the bound-continuum vibrational predissociation model for Van der Waals molecule dissociation (half collisions) to a continuum-continuum vibrational predissociation model for the full collisions.

#### HCl<sup>+</sup> REACTIONS WITH SF<sub>6</sub> AND CF<sub>4</sub>.

The reaction :



occurs on every collision, implying  $\text{AE}(\text{SF}_5^+/\text{SF}_6) < 14.17$  eV. Analysis of this data and that of Richter et al<sup>8</sup> who found  $\text{Kr}^+(\text{}^2\text{P}_{3/2})$  to react with SF<sub>6</sub> to produce SF<sub>5</sub><sup>+</sup>, measurements<sup>9</sup> showing  $\text{IP}(\text{SF}_5) < 10.16$  eV and  $\text{D}(\text{SF}_5 - \text{F}) = 3.95 \pm 0.14$  eV<sup>10</sup> lead to values  $\text{AE}(\text{SF}_5^+/\text{SF}_6) = 13.98 \pm 0.03$  eV and  $\text{D}(\text{SF}_5 - \text{F}) < 3.9$  eV<sup>11</sup>. Similarly the reaction



was found to be nearly thermoneutral and  $\text{AE}(\text{CF}_3^+/\text{CF}_4) = 14.2 \pm 0.1$  eV was determined<sup>12</sup>. Values of both AE's in the literature are much higher ~ 15.5 eV.

#### HBr<sup>+</sup> REACTIONS

Proton transfer reactions of HBr<sup>+</sup> with CO<sub>2</sub>, CH<sub>4</sub>, CF<sub>4</sub>, N<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, COS and H<sub>2</sub>S have been measured. An analysis of these data appears to provide a resolution of the current controversy over the absolute proton affinity scale in the ~ 120-150 kcal mol<sup>-1</sup> proton affinity range.



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## SIFT STUDIES OF THE REACTIONS OF $N_4^+$ IONS WITH $H_2$ , $D_2$ , AND Ar \*

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### ABSTRACT

The reactions of  $N_4^+$  with  $H_2$ ,  $D_2$ , and Ar and  $N_2Ar^+$  with  $N_2$  have been studied as a function of centre-of-mass interaction energy,  $E_{cm}$ , in helium carrier gas using an SIFT apparatus. The rate coefficient for each of the reactions increases with  $E_{cm}$ . From the data, activation energies for the  $N_4^+ + H_2$ ,  $D_2$ , and Ar reactions have been obtained and are consistent with those previously determined in a truly thermal flowing afterglow experiment. From a consideration of the rate coefficients for the  $N_4^+ + Ar$  and the reverse  $N_2Ar^+ + N_2$  reactions, estimates have been made of the enthalpy and entropy changes in the reactions, the former parameter relating to the difference between the bond energies of  $N_4^+ - N_2$  and  $N_2^+ - Ar$ . From the entropy change, together with a consideration of the partition functions of the reactants and products, the structure of  $N_2Ar^+$  has been derived. The results of this study have been carefully compared with previous work.

### INTRODUCTION

That  $N_4^+$  is a stable positive ion has been appreciated for many years [1]. It is readily formed in nitrogen-rich ionized gases (even at moderate pressures) by three-body (ternary) association of  $N_2^+$  with  $N_2$ . The ternary association reaction rate coefficient has been measured in both  $N_2$  and He bath gases as a function of temperature in several laboratories (see ref. 2 and the references cited therein). Much interest has centred on its binding energy

\* Dedicated to Eldon E. Ferguson in honour of his contributions to ionic physics and chemistry.

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[equivalently the dissociation energy  $D(N_2^+ - N_2)$ ]. Perhaps the most reliable experimental determinations are those from equilibria studies due to Teng and Conway [3] which gives  $D_0^0(N_2^+ - N_2)$  as  $1.12 \pm 0.1$  eV ( $D_{298}^0 = 1.06$  eV) and from Paysant and Kébarle [4] for which  $D_{298}^0 = 0.99$  eV. Also a value of  $0.9 \pm 0.2$  eV has been deduced from the appearance energy of  $N_4^+$  generated in electron collisions with  $(N_2)_2$  dimers [5]. Since the first experimental observation of  $N_4^+$ , theorists have been interested in determining its geometry [6,7] and the electronic states which are responsible for its sizable binding energy. Detailed structure calculations [7] have indicated that the linear conformation of the N atoms is the most stable and a binding energy of 1.32 eV has been calculated.

It is also known that  $N_4^+$  ions are involved in the ion chemistry of the Earth's lower atmosphere [8], an exciting area of ion chemistry to which Eldon Ferguson has contributed so much. Hence, a good deal of attention has been given to its reactions with atmospheric and other gases [9,10]. Amongst the many reactions of  $N_4^+$  which have been studied, that with  $H_2$  is most unusual



This reaction is quite exothermic (by 1.5 eV) yet at 300 K, the rate coefficient  $k(1)$  is only  $2.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  compared with the collisional rate coefficient for the reaction,  $k_2(1)$ , which is  $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Also,  $k(1)$  increases dramatically with increasing temperature, as revealed by variable-temperature flowing afterglow (FA) studies in helium carrier gas, and with increasing  $N_4^+ \cdot H_2$  centre-of-mass energy, as has been revealed by the flow drift tube (FDT) studies in  $N_2$  carrier gas. Both studies were carried out in Ferguson's laboratory at NOAA [9]. These co-ordinated FA and FDT studies also included the analogous reaction



which exhibited similar behaviour.

This work raised the question whether it is the translational energy increase between the reactants or the enhanced internal energy of the  $N_4^+$  ion which so efficiently promotes reactions (1) and (2). Since these measurements were carried out, a greater understanding has developed of the importance of vibrational excitation of molecular ions in drift tubes and flow drift tubes [11] and of how such excitation can influence ion-molecule reactions [12]. This has been possible due to the development of the selected ion flow tube (SIFT) [13] and the selected ion flow drift tube (SIFDT) [14]. In these techniques, the ion source gas (i.e.  $N_2$  for  $N_4^+$ ) is excluded from the flow tube and therefore cannot interact with (e.g. vibrationally quench) the  $N_4^+$ , for example following its excitation in collisions with the carrier gas

atoms or molecules during its acceleration in a drift field (such an interaction with the source gas could have been occurring in the FA and FDT experiments described above). In a recent SIFDT study at Birmingham [15],  $N_4^+$  ions were generated in a high-pressure electron impact ion source containing  $N_2$ , injected into helium carrier gas and accelerated in the drift field of the SIFDT. At  $N_4^+/\text{He}$  centre-of-mass energies below  $D(N_4^+ - N_2)$ , dissociation of the  $N_4^+$  to  $N_2^+$  was observed. This is a clear indication that vibrational excitation of the  $N_4^+$  occurs in the  $N_4^+/\text{He}$  carrier gas collisions. This conclusion was reinforced by the fact that, when isotopically labelled  $N_2$  was added to the flow tube, the exchange of  $N_2$  molecules in  $N_4^+/\text{N}_2$  collisions became facile at elevated  $N_4^+/\text{He}$  centre-of-mass energies. That vibrational excitation of  $N_4^+$  occurs in He collisions strongly implies that vibrational excitation will be very efficient in  $N_4^+/\text{N}_2$  collisions, a conclusion reached previously by the NOAA group [9].

In pursuit of a better understanding of the variation of  $k(1)$  and  $k(2)$  with energy, we have carried out a detailed study of reactions (1) and (2) using the Aberystwyth SIFDT. This has been possible using a high-pressure ion source based on a design by Paulson and Dale [16] from which we have been able to inject into the flow tube substantial  $N_4^+$  currents at energies sufficiently low that significant break-up of the  $N_4^+$  did not occur. This facility has enabled us to study the near-thermoneutral reaction



and also the reverse process



since the ion source also provided substantial yields of  $N_2\text{Ar}^+$ . Teng and Conway [3] have studied mass spectrometrically the equilibrium ratios of the  $N_4^+$  to  $N_2\text{Ar}^+$  ion signals in a variable-temperature drift tube containing controlled mixtures of nitrogen and argon, from which they have deduced the mean enthalpy change,  $\Delta H^\circ$ , in reaction (3) to be 0.04 eV over the temperature range 300–700 K. This implies that  $D(N_2^+ - \text{Ar})$  is slightly greater than  $D(N_4^+ - N_2)$ . Our SIFDT kinetic data for reactions (3) and (4) also provide information on  $\Delta H^\circ$  and  $\Delta S^\circ$  (see the Results and Discussion section).

#### EXPERIMENTAL

The SIFDT technique has been described in detail in previous publications [13,14,17]. Worthy of note here is the structure of the very efficient venturi-type inlet (such inlets are essential features in all SIFT and SIFDT apparatuses [14]) recently included in the Aberystwyth SIFDT through

which ions, generated in a remote ion source, enter the flow tube. Essentially, it consists of an annular slit which surrounds the ion entrance aperture and of two sets of small circular apertures located on larger pitch circle diameters. Carrier gas flows through the slit and through the circular apertures from a common reservoir. The relative areas of the slit and the apertures are such that only a very small fraction of the carrier gas flows through the slit. With this venturi arrangement (which is a hybrid of the Birmingham design and the NOAA/York design described in refs. 14 and 18) and the efficient high-pressure ion source [16], substantial currents of  $N_4^+$  could be injected into the flow tube at energies sufficiently low to prevent break-up of the ion in collisions with helium carrier gas (a  $N_4^+/\text{He}$  centre-of-mass energy  $< 0.8$  eV was necessary). Thus  $N_4^+$  count rates as large as  $10^4$  counts  $s^{-1}$  were recorded at the downstream detector in the SIFDT. Similar count rates of  $N_2Ar^+$  could be obtained by forming  $N_2Ar^+$  in the ion source using a mixture of  $N_2$  and Ar as the source gas.

In order to measure rate coefficients in the SIFDT, it is necessary to determine the reaction (residence) time of the ions at each value of  $E/N$  (the ratio of the electric field strength,  $E$ , to carrier gas number density,  $N$ ) for which the  $k$  is required. A convenient way is first to measure the mobility,  $\mu$ , of the particular ion species as a function of  $E/N$  prior to the measurement of  $k$ . The procedure for measuring  $\mu$  in the Aberystwyth SIFDT has been described previously [17,19]. Thus, we measured  $\mu$  for both  $N_4^+$  and  $N_2Ar^+$  in room-temperature helium at a pressure of 0.25 torr for values of  $E/N$  up to 100 Townsends (100 Td). The results are shown

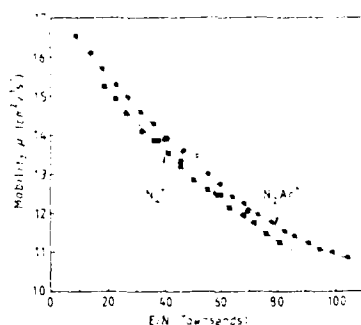


Fig. 1. Reduced mobilities,  $\mu$ , as a function of  $E/N$  for  $N_4^+$  and  $N_2Ar^+$  ions drifting in pure He carrier gas in the SIFDT from measurements at a He pressure of about 0.25 torr and at a temperature of 300 K. These  $\mu$  data are used in the calculation of the rate coefficients and centre-of-mass energies presented in the other figures.

graphically in Fig. 1 where it can be seen that  $\mu(\text{N}_2\text{Ar}^+)$  somewhat exceeds  $\mu(\text{N}_4^+)$  over the complete  $E/N$  range. The difference in mobility is presumably due, in part, to the larger size of  $\text{N}_4^+$  (4.09 Å long) compared with that of  $\text{N}_2\text{Ar}^+$  (2.23 Å long, see below). The precision of these measurements of  $\mu$  ( $\pm 4\%$ ) exceeds those for other ion types previously measured by the Aberystwyth group due to the use of a multichannel scaler with a 1  $\mu\text{s}$  time resolution. The rate coefficients of reactions (1)–(4) were then measured in the usual way at a number of  $E/N$  values for each reaction using the  $\mu$  values to calculate the reaction times and also the reactant ion/reactant molecule and the reactant ion/helium carrier gas centre-of-mass energies,  $E_r$  and  $E_c$ , respectively. These energies are readily obtained using the Wannier relationship, as has been described in many publications [20,21].

#### RESULTS AND DISCUSSION

The measured rate coefficients  $k(1)$  and  $k(2)$  for the reactions of  $\text{N}_4^+$  with  $\text{H}_2$  and  $\text{D}_2$ , respectively, are shown in Fig. 2 plotted as a function of the  $\text{N}_4^+/\text{H}_2$  and  $\text{N}_4^+/\text{D}_2$  centre-of-mass energies,  $E_r$ . Also represented in Fig. 2 for comparison are the data of Lindinger et al. [9] obtained in  $\text{N}_2$  carrier gas.

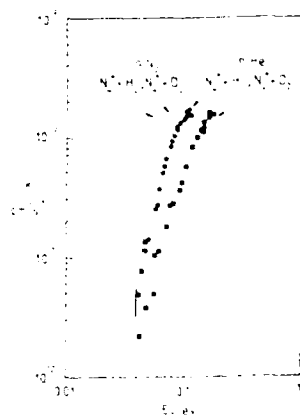


Fig. 2. The rate coefficients,  $k$ , as a function of  $E_r$  for the reactions of  $\text{N}_4^+$  with  $\text{H}_2$  (●) and  $\text{N}_4^+$  with  $\text{D}_2$  (■) in He carrier gas at 300 K. The continuous lines represent the previous data (from ref. 9) for the same reactions but in  $\text{N}_2$  carrier gas. The more rapid rise of  $k$  with  $E_r$  in the  $\text{N}_2$  carrier gas is attributed to the occurrence of vibrational excitation of the  $\text{N}_4^+$  in collisions with  $\text{N}_2$  carrier gas molecules.

These reactions are exothermic by 1.5 eV and so the very rapid increase in  $k(1)$  and  $k(2)$  with  $E_r$  is indicative of an energy barrier to the reaction. Hence, given in Fig. 3 are the drift tube equivalents of Arrhenius plots of the data ( $k$  versus  $E_r^{-1}$ ). The linearity of these plots indicates that an Arrhenius-type law [i.e.  $k = A \exp(-3 \Delta E/2 E_r)$ ] represents these data quite well and the activation energies,  $\Delta E$ , obtained from the slopes of the lines are  $0.157 \pm 0.01$  eV for the  $H_2$  reaction (1) and  $0.169 \pm 0.01$  eV for the  $D_2$  reaction (2). The  $\Delta E$  derived for reaction (1) is in very good agreement with the truly thermal value previously obtained from the variation of  $k(1)$  with temperature [9], which is not subject to the doubts inherent in determining  $\Delta E$  values from non-thermal drift tube experiments. This agreement between the  $\Delta E$  obtained in the two different experiments indicates that, in the present SIFDT experiments in helium carrier gas over the small  $E_r$  range from 0.04 to about 0.1 eV, any departures of the rotational, vibrational populations of the  $N_4^+$  ions and the rotational populations of the  $H_2$  molecules from their thermal equilibrium values at a temperature  $T_r$ , given by  $E_r = (3/2) k T_r$ , does not significantly influence the rate of the reaction. Presumably these remarks also apply to the deuterium reaction (2). Note, however, that the more rapid increase in  $k(1)$  and  $k(2)$  with  $E_r$  as observed in the  $N_2$  carrier gas (see Fig. 2) has been attributed to the vibrational excitation of the  $N_4^+$  ions, which is efficiently induced by collisions with the heavy  $N_2$  carrier gas

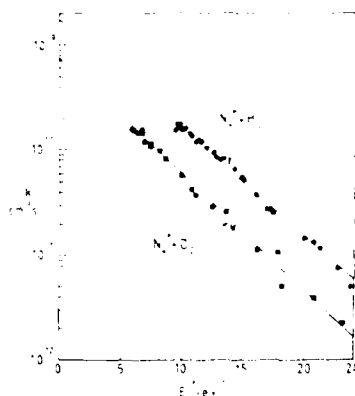


Fig. 3. "Arrhenius plots" ( $k$  versus  $E_r^{-1}$ ) of the data obtained in He carrier gas and given in Fig. 2. The activation energies for the reactions obtained from the slopes of these lines are given in the text.

molecules [9]. It is clear that vibrational excitation of the  $N_4^+$  also occurs in the helium carrier gas at high  $E/N$  since the  $N_4^+$  actually dissociates (see the Introduction), but it is obviously much less efficient in He collisions than in  $N_2$  collisions.

The small difference between the values of  $\Delta E$  for the  $H_2$  and  $D_2$  reactions is barely significant within the errors of the experiments and may, in part, be due to the non-thermal nature of the drift tube experiments, although an isotope effect on  $\Delta E$  is to be expected because of the differences in the zero-point energies (and thus in the barrier heights) within the hydrogenated and deuterated intermediate complexes formed in the reactions. However, the differences in the magnitudes of  $k(1)$  and  $k(2)$  at the same  $E_r$  require some comment. This difference is greatest at low  $E_r$  where the ratio  $k(1)/k(2)$  is about 3.5, but from an extrapolation to the high-energy limit of  $E_r$  (i.e. where  $E_r^{-1} \rightarrow 0$ , see Fig. 3) the ratio is about 2.5. In part, these ratios are explained by the differences in the collisional rate coefficients for the reactions for which  $k_0$  is  $1.51 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for reaction (1) and  $1.08 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for reaction (2), i.e. a ratio of 1.4. So the value of 2.5 for  $k(1)/k(2)$  when  $E_r^{-1} \rightarrow 0$  is presumably accounted for by the 1.4 factor and a similar factor resulting from an isotope effect, the origin of which is probably a small difference in the barrier heights to H and D transfer within the  $N_4^+ \cdot H_2$  and  $N_4^+ \cdot D_2$  complexes. It should be noted that, in the analogous experiments carried out by Lindinger et al. [9] in  $N_2$  carrier gas, the observed ratio of  $k(1)/k(2)$  changed from about 2.5 at low  $E_r$  to 1.3 at the highest values of  $E_r$ , but this system, unlike the helium carrier gas system, does not approximate to the truly thermal system, especially at high  $E_r$  at which the  $N_4^+$  is surely highly vibrationally excited.

The rate coefficients for both the  $N_4^+ + \text{Ar}$  reaction (3) and the  $N_2\text{Ar}^+ + N_2$  reverse reaction (4) increase rapidly with  $E_r$  as is shown in Fig. 4. Measurements were made at  $E_r$  values up to about 1 eV for both reactions. However, it was observed that  $E_r$  values in excess of about 0.3 eV initiated the break-up of  $N_2\text{Ar}^+$  ions (almost exclusively to  $N_2^+$  and Ar) and so data relating to reaction (4) above 0.3 eV are not included in Fig. 4. The data for reaction (3) are plotted in Fig. 5 as an Arrhenius-type plot of  $\ln k(3)$  versus  $E_r^{-1}$  and, as is obvious, a non-linear plot results, unlike those in Fig. 3 for the  $N_4^+$  reactions with  $H_2$  and  $D_2$ , even though the experiments were carried out over very similar  $N_4^+ \cdot \text{He}$  centre-of-mass energies,  $E_c$ . (The  $E_r$  values in the case of the reactions of  $N_4^+$  with the heavier Ar are much greater than the  $E_r$  for the  $N_4^+$  reactions with the lighter  $H_2$  and  $D_2$ , even though the  $E_c$  values are similar). The up-curving of the plot in Fig. 5 at small  $E_r^{-1}$  is presumably due to the vibrational excitation of the  $N_4^+$  ions during their collisions with Ar atoms. If the data points above an  $E_r^{-1}$  value of  $3 \text{ eV}^{-1}$ , for which  $N_4^+$  is observed to begin to break-up, are represented by a straight



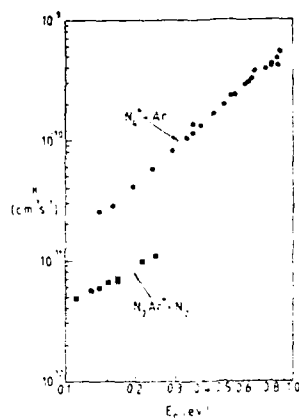


Fig. 4. The rate coefficients,  $k$ , for the reactions of  $N_4^+$  with Ar and  $N_2Ar^+$  with  $N_2$  as a function of  $E_e$  in He carrier gas at 300 K. The increase in  $k$  with  $E_e$  is attributed to activation energy barriers in both reactions (see text and Fig. 5). These data are plotted in the form of a van't Hoff plot in Fig. 6.

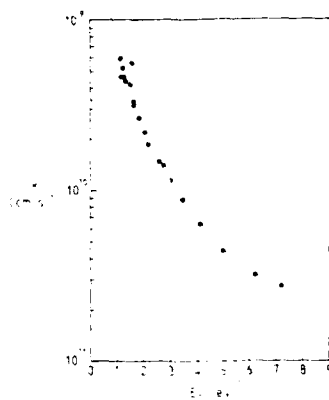


Fig. 5. An "Arrhenius plot" ( $k$  versus  $E_e^{-1}$ ) of the data given in Fig. 4 for the reaction of  $N_4^+$  with Ar. The solid line represents the data obtained previously, also in a drift tube [22]. The departure of the points from the line at low  $E_e^{-1}$  is attributed to the enhancement of  $k$  due to vibrational excitation of the  $N_4^+$  at high  $E_e$ .

line as shown, then this indicates an activation energy barrier,  $\Delta E$ , to the reaction of about 0.26 eV which is essentially the same as that obtained by the Innsbruck group from their recent drift tube study of reaction (3) [22]. Also, the value of  $k(3)$  obtained by extrapolating the line in Fig. 5 to zero  $E_r^{-1}$  is  $\sim 3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , again the same as that obtained previously [22]. This value is a factor of two smaller than the collisional limiting value of  $6.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .

Reactions (3) and (4) are the exact reverse of each other and so the ratio  $k(3)/k(4)$  can be equated to an equilibrium constant. Thus a van't Hoff plot of  $\ln k(3)/k(4)$  versus  $E_r^{-1}$  is shown in Fig. 6 for  $E_r^{-1}$  values greater than 3  $\text{eV}^{-1}$ . The slope of the plot indicates a mean enthalpy change,  $\Delta H^\circ$ , of  $0.09 \pm 0.01 \text{ eV}$  over the  $E_r$  range from 0.1 to 0.25 eV and an entropy change,  $\Delta S^\circ$ , of  $19 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ . This small positive value of  $\Delta H^\circ$  contrasts with the small negative value, already quoted, of  $-0.04 \text{ eV}$  obtained by Teng and Conway [3]. The difference could be due to several reasons including the different energy regimes over which the experiments were performed. In the SIFDT experiment, it cannot be excluded that some collisional excitation of the ions occurred, even at the low  $E_r$  used; differential excitation of the  $\text{N}_2^+$  and  $\text{N}_2\text{-Ar}^+$  would obviously be manifest as an erroneous  $\Delta H^\circ$ . In the Teng and Conway experiment, competing ionic reactions in the  $\text{N}_2\text{-Ar}$  mixtures could complicate the interpretation of data. The present SIFDT data indicates that  $D(\text{N}_2^+ - \text{N}_2)$  is somewhat greater than  $D(\text{N}_2^+ - \text{Ar})$ , contrary to the conclusion drawn from the Teng and Conway data. Further experiments are necessary to resolve this uncertainty.

The derived  $\Delta S^\circ$  value from the present SIFDT data compares with  $15 \text{ J mol}^{-1} \text{ K}^{-1}$  obtained by Teng and Conway. It is worth noting that errors in

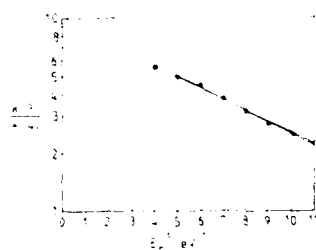


Fig. 6. A "van't Hoff plot" [ $\ln k(3)/k(4)$  versus  $E_r^{-1}$ ] of the data for the  $\text{N}_2^+ - \text{Ar}$  reaction (3) and the  $\text{N}_2\text{-Ar}^+ - \text{N}_2$  reaction (4) from Fig. 4 for  $E_r$  values less than 0.25 eV. Above this  $E_r$  value, vibrational excitation of the ions occurred. The slope of the plot yields a value of  $\Delta H^\circ = 0.09 \pm 0.01 \text{ eV}$  and the intercept yields a value of  $\Delta S^\circ = 19 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ .

this  $\Delta S^\ddagger$  can result from mass discrimination in the mass spectrometer of the drift tube experiments. This is not the case in the SIFT experiment, which is concerned only with kinetic measurements and not relative ion signal levels.) The experimentally determined  $\Delta S^\ddagger$  is useful in that it can be used to determine the approximate structure of the  $\text{N}_2\text{Ar}^+$  ion. The information required to calculate  $\Delta S^\ddagger$  in reactions (3) or (4) is all available except for the structure of  $\text{N}_2\text{Ar}^+$  (note that Teng and Conway [3] favour a linear structure for this ion, based on the shapes of the molecular orbitals, although they could not rule out the possibility that the molecule is T-shaped). It is known that  $\text{N}_4^+$  is linear and the bond lengths between the N atoms in the ion have been determined by ab initio methods [3] and so its moment of inertia can be readily calculated.  $\text{N}_4^+$  is also known to have a  $^2\Sigma^+$  configuration in the ground state [5] and, obviously, a symmetry number of 2 is appropriate to this ion.  $\text{N}_2\text{Ar}^+$  can be shown to be  $^2\Sigma^+$  by correlation of electronic states [23]. Clearly, all the necessary information is readily available for the Ar atom and the  $\text{N}_2$  molecule and so an expression can be obtained for  $\Delta S^\ddagger$  in the reaction in terms of the total partition functions of the species involved (which includes translational, rotational, and electronic contributions; see, for example, ref. 24), the only unknown being the moment of inertia of  $\text{N}_2\text{Ar}^+$ . Thus, by then equating the theoretical expression for  $\Delta S^\ddagger$  to the experimental value, an estimate can be obtained for the moment of inertia of the ion and the value arrived at is  $55 \text{ u } \text{\AA}^2$  on the assumption that it is the *linear* species  $[\text{N}-\text{N}-\text{Ar}]^+$ . It is apparent that the ion cannot be *non-linear* since this would result in derived moments of inertia some two orders of magnitude smaller than that of  $\text{N}_4^+$ , which is calculated to be  $143 \text{ u } \text{\AA}^2$  and, in the light of this, the derived value for linear  $\text{N}_2\text{Ar}^+$  seems to be very reasonable. Assuming that the N-N bond length,  $a$ , in  $\text{N}_2\text{Ar}^+$  is the same as those in the  $\text{N}_2^+-\text{N}_2$  ion (i.e.  $\text{N}^+\text{N}^+\text{N}^+\text{N}$ ,  $a = 1.08 \text{ \AA}$ ,  $b = 1.93 \text{ \AA}$  [7]), then the N-Ar bond length,  $c$ , is calculated to be  $1.15 \text{ \AA}$  (i.e.  $\text{N}^+\text{N}^+\text{Ar}$ ), not an unreasonable result. Clearly, these conclusions could be tested by structure calculations. In support of the assumption that the N-N bond length in  $\text{N}_2\text{Ar}^+$  is the same as that in  $\text{N}_4^+$ , it is worthy of note that Baker and Buckingham [25] have calculated the N-N bond length in  $\text{N}_2\text{CO}^+$  to be  $1.08 \text{ \AA}$ .

#### CONCLUDING REMARKS

The exothermic reactions (1) and (2) and the near-thermoneutral reactions (3) and (4) are all slow at room temperature but all become more efficient as the centre-of-mass energies of the reactants,  $E_r$ , increase. It is evident that small activation energy barriers are inhibiting all of these reactions, barriers which can be overcome by increased  $E_r$  and also by vibrational excitation in

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